The University of Chicago

NEUTRALIZATION AND IONIZATION OF HIGH-VELOCITY IONS OF NEON, ARGON, AND KRYPTON BY COLLISION WITH SIMILAR ATOMS

A DISSERTATION SUBMITTED TO THE FACULTY OF THE DIVISION OF THE PHYSICAL SCIENCES IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

1933

By

HAROLD FRANCIS BATHO

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Neutralization and Ionization of High-Velocity Ions of Neon, Argon and Krypton by Collision with Similar Atoms

By HAROLD F. BATHO
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Rudnick's work on the measurement of the free path L_0 for the ionization of a helium atom and the free path L_1 for neutralization of a helium ion in helium, has been extended to the gases neon, argon, and krypton for the velocity range corresponding to accelerating potentials of 10,000 to 22,000 volts. With neon, the work has covered the pressure range from 0.75×10^{-2} mm to 4×10^{-2} mm; with argon, from 0.30×10^{-2} mm to 1.6×10^{-2} mm; and with krypton, from 0.30×10^{-2} mm to 1.4×10^{-2} mm. In all cases, the free path for ionization, reduced to 760 mm pressure, is found to be approximately 6.5×10^{-4} cm. For neon, the free path for neutralization is 0.95×10^{-4} cm; for argon, 0.45×10^{-4} cm; and for krypton, 0.35×10^{-4} cm. Both free paths decrease with increasing velocity. The fraction F_∞ of neutral atoms in the beam when the equilibrium condition is reached is approximately 0.86 for neon, 0.93 for argon, and 0.95 for krypton. This fraction decreases with increasing velocity for neon and argon but appears to increase slightly for krypton. The observed dependence of the free paths on pressure is compared with the theoretical dependence. The results obtained are compared with the low-velocity measurements of other workers and the differences discussed. The relationship of this work to Doppler effect experiments with neon and argon is considered.

THE free paths of the positive ions of hydrogen,[1] helium,[1,2] neon,[1] and argon[1,3,4] have been measured by several investigators for velocities corresponding to accelerating potentials of less than 1000 volts. In the cases of hydrogen[5,6,7,8,9,10] and helium[11] the measurements have been extended to the voltage range from 5000 to 25,000 volts. The high-velocity work has included measurements of the free paths of the neutral atoms and determination of the fraction of neutral particles in the total beam when an equilibrium is established between the neutral and charged particles. Similar measurements with neon, argon, and krypton for high velocities (10,000 to 22,000 volts) have seemed of interest for comparison with the low-voltage measurements, and of importance in view of the unexpected absence of displaced arc lines in Doppler effect observations of the positive rays of neon[12,13] and argon[13,14].

[1] H. Kallmann and B. Rosen, Zeits. f. Physik **61,** 61 (1930).
[2] A. J. Dempster, Phil. Mag. **3,** 115 (1927).
[3] Penning and Veenemans, Zeits. f. Physik **62,** 746 (1930).
[4] F. Wolf, Phys. Zeits. **32,** 897 (1931).
[5] W. Wien, Sitz. d. K. P. Akad. d. Wiss., July, 1911, p. 773.
[6] J. Koenigsberger and J. Kutschewski, Ann. d. Physik **37** 161 (1912).
[7] A. Rüttenauer, Zeits. f. Physik **4,** 267 (1921).
[8] E. Rüchardt, Ann. d. Physik **71,** 377 (1923).
[9] H. Bartels, Ann. d. Physik **6,** 957 (1930).
[10] F. Goldmann, Ann. d. Physik **10,** 460 (1931).
[11] P. Rudnick, Phys. Rev. **38,** 1342 (1931).

Wien[5] and Rüchardt[15] have shown that if F represents the fraction of neutral particles in the total beam, assuming a simple exchange of electrons between moving and rest particles without appreciable change of velocity or direction of the moving particles, the value of F at a distance x from the point of origin of the beam is

$$F = F_\infty + (F_0 - F_\infty)e^{-(1/L_0+1/L_1)xp} \tag{1}$$

where F_0 is the neutral fraction at the point of origin, F_∞ the neutral fraction when an equilibrium is established between neutral and charged particles, $p\,dx/L_0$ the probability of ionization of a neutral atom in a distance dx, and $p\,dx/L_1$ the probability of neutralization of an ion in the same distance. L_0 may be interpreted as the mean free path for ionization of an atom and L_1 the free path for neutralization of an ion for unit pressure. Since the ratio

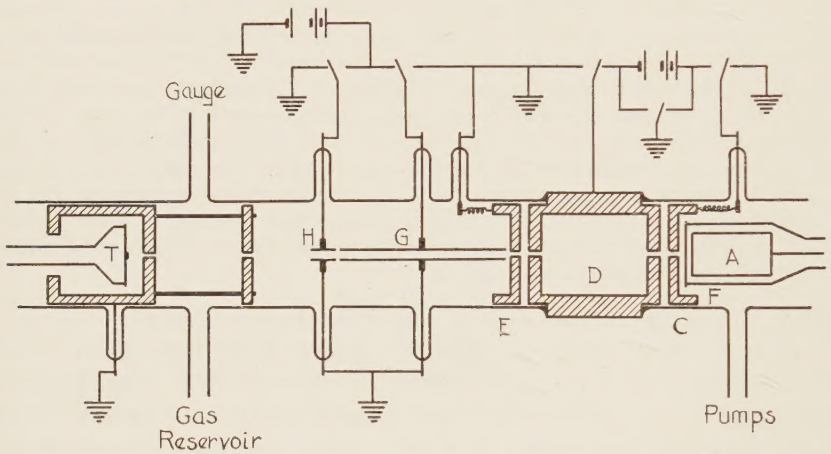

Fig. 1. Diagram of apparatus. A, anode; C, D, and E, accelerating electrodes; F, hot cathode; G, and H, deflecting condensers. T, thermocouple.

of the number of neutral to the number of charged particles in the equilibrium condition of the beam is inversely proportional to the probability of change,

$$F_\infty = L_0/(L_0 + L_1). \tag{2}$$

From Eqs. (1) and (2) it is seen that, provided F_0, p, and x are known, two measurements of F are sufficient for the determination of L_0, L_1, and F_∞. In practice, to observe F, the total intensity of the beam is measured; then, a transverse electric field is applied at the point x to remove the positive ions, allowing a measurement of the intensity of the remaining neutral atoms. In order to obtain the true value of F, the ratio of neutral intensity to total intensity thus obtained must be corrected for the finite length of the field since the field not only removes all ions already present at the point chosen

[12] W. Romig, Phys. Rev. **38**, 1709 (1931).
[13] A. I. McPherson, Phys. Rev. **41**, 686 (1932).
[14] K. Friedersdorff, Ann. d. Physik **47**, 737 (1915).
[15] R. Rüchardt, Handb. d. Physik **XXIV**, p. 90.

but also removes all ions formed along its length before they have time to return to the neutral state. If the field is applied along a length y of the path of the beam, there will be a simple exponential decay of intensity due to neutrals becoming positive given by

$$I = I_0 e^{-py/L_0} \tag{3}$$

where I_0 is the intensity of the neutrals at the beginning of the field, and I the intensity of the neutrals actually observed. Therefore, the measured ratio must be corrected by the factor e^{py/L_0} to give the true value of F at the beginning of the field.

Experimental Arrangement

The experimental arrangement used, shown in Fig. 1, was almost identical with that used by Rudnick.[11] Ions of the desired gas were formed in a low-voltage arc, by maintaining a small potential difference between the hot filament F and the hollow anode A. The heating current for the filament and the arc potential were supplied by storage batteries. For reasons to be mentioned shortly these batteries were insulated from ground. The filament F and electrode C were maintained at the same potential so that some of the ions formed were drawn through the circular opening in C where they were accelerated by the desired potential difference between C and D. Thus, a beam of high velocity particles proceeded to the thermocouple T. In Doppler effect experiments using this method of producing positive rays, it has been found that very sharp, displaced lines are obtained,[13,16] indicating that the ions are quite homogeneous in velocity.

For some of the measurements, a beam of particles, which were initially all positive, was required. In this case A, F, and C were raised to a high positive potential with D and E grounded. For other measurements a beam initially neutral was obtained by grounding F, C, and E, and raising D to a high negative potential. With this arrangement the ions were accelerated between C and D. In D they changed charge by collision with gas atoms. All ions remaining in the beam at the end of D were stopped by the retarding field between D and E, allowing only neutral atoms to proceed beyond E. In either case, deflecting fields could be applied along either G or H to remove all ions formed, allowing the measurement of the ratio (uncorrected) of the neutral intensity to the total intensity of the beam.

All cross-hatched parts in Fig. 1 were turned from rolled brass; the anode A was made of nickel; the plates of the condensers G and H of nickel gauze. The electrode D was 5.7 cm in length; G, 7.4 cm; and H, 1.1 cm. The total distance from C to the thermocouple was 24 cm. The thermocouple and the filament and anode were carried on ground joints to facilitate the alignment of the couple and the replacement of the filament. Wax joints were used between the two glass ends of the tube and the center electrode D to permit the easy adjustment and replacement of the electrodes C, D and E.

In all cases it was desirable to have only singly charged ions present. In order to ensure this the arc potential used to form the ions was always less

[16] H. F. Bathe and A. J. Dempster, Astrophys. J. **75**, 34 (1932).

than the second ionizing potential of the gas in which the measurements were being taken. Doubly charged ions might be formed by collision in passage through the gas but the absence of any displaced lines due to doubly charged particles in Doppler effect experiments with neon and argon,[13] even though no precautions are taken regarding the arc voltage, seems to indicate that the number of doubly charged ions present in the beam is negligible for the pressures and velocities used.

The retarding field used to stop the positive ions, in measurements with an initially neutral beam, accelerated electrons toward the thermocouple. To avoid rather large errors due to this cause, it was necessary to use a transverse magnetic field of sufficient intensity to deflect the electrons, but small enough not to deflect the positive ions appreciably.

It was found that, above 1600 volts, increasing the potential difference across the deflecting condenser did not change appreciably the intensity as measured by the thermocouple; accordingly, this deflecting potential was used to remove all ions from the beam.

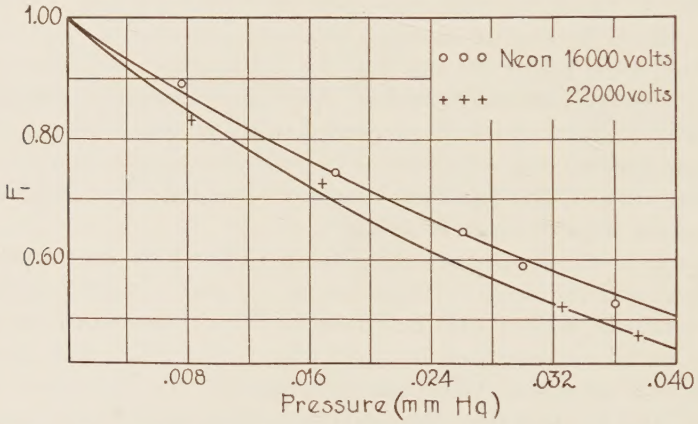

Fig. 2. Relationship between F_1 and pressure. Points shown are experimental values, curves are values plotted from Eq. (4).

The thermocouple was a junction formed by spot-welding 3 mil platinum wire and 10 mil extruded bismuth wire to a platinum foil target 1 mm^2 in area. The other ends of the wires were joined to nickel lead wires, also by means of platinum foil. The thermoelectric current was indicated by a low-resistance galvanometer of sensitivity 168 megohms. To avoid errors in the measurement of intensity it was found necessary to shield the thermocouple rather carefully. The hot filament was placed slightly off the axis of the tube and the anode was made hollow, thus reducing the amount of radiation reaching the thermocouple directly from the arc in which the ions were formed. The considerable thickness of brass between filament and thermocouple also served the same purpose. Fluctuations in room temperature caused irregular changes in the zero reading of the galvanometer, i.e., in the reading of the galvanometer when no particles were striking the target of the thermocouple. This difficulty was eliminated by enclosing the entire thermocouple end of

the tube in a large asbestos cylinder. After this precaution had been taken, it was found that the zero reading shifted only very slowly.

On account of the wax seals it was not possible to bake out the tube before admitting the gas to be used. However, the exhausting pumps were run at intervals over a period of two or three days before gas was admitted in an attempt to eliminate occluded vapors and gases. With the gases used it was not considered feasible to maintain a steady flow of gas. The neon was admitted to the tube through an adjustable lavite valve,[17] and, after entering the tube, was circulated over charcoal immersed in liquid air. The circulating pump was shut off while readings were being taken to avoid pressure differences along the path of the beam but the gas was circulated at frequent intervals between runs. This appeared sufficient to maintain the purity of the gas. The argon and krypton were purified in the reservoir before entering the tube, by evaporating magnesium in a side tube by means of a high-frequency induction heater. In all cases, a liquid air trap was placed in close connection

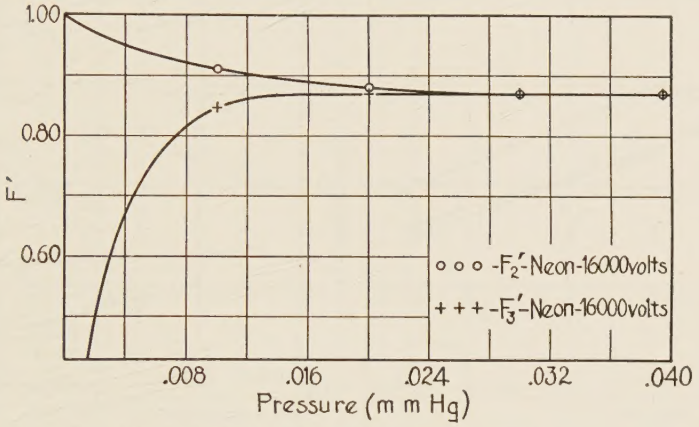

Fig. 3. Relationship between F' and pressure.

with the main tube to eliminate, if possible, vapors of mercury, stopcock grease, and wax. The leads from the reservoir, to the McLeod gauge on which pressures were read, and to the exhausting pump, passed through liquid air traps. During the period in which readings were taken, liquid air was kept on these traps continuously to prevent diffusion of mercury vapor into the tube. These precautions having been taken, the spectrum of the gas in the tube, as examined with a small hand spectroscope, failed to show any mercury lines. As will be seen later, however, there is reason to doubt that these precautions were sufficient to eliminate vapors entirely.

Measurements and Results

For each pressure and voltage three ratios were determined. The first two measurements were made with an initially neutral beam (C and E grounded,

[17] This valve consisted of a lavite cone partially covered with mercury so arranged that the rate of leak could be controlled by changing the mercury level by means of a magnetically operated soft iron plunger. The valve worked very satisfactorily for the purpose for which it was used. The lavite cone was very kindly furnished by the American Lava Corporation.

D at a high negative potential). The first, F_1, was the ratio of the number of particles reaching the thermocouple, when a deflecting field was applied to the long condenser G only, to the number of particles reaching T with no field applied; the second, F_2, was a similar ratio with the deflecting field applied to the short condenser H instead of G. The third measurement, F_3, differed from the second only in the fact that an initially positive beam was used. For each voltage the three ratios were measured at a series of pressures so that curves could be plotted showing the dependence of each ratio on pressure. With all three gases, the measurements covered the voltage range from 7000 to 22,000 volts. With neon, the pressure range was from 0.75×10^{-2} to 4.0×10^{-2} mm of mercury; with argon, from 0.30×10^{-2} to 1.6×10^{-2} mm; with krypton, from 0.30×10^{-2} to 1.4×10^{-2} mm. The lower limits for both velocity

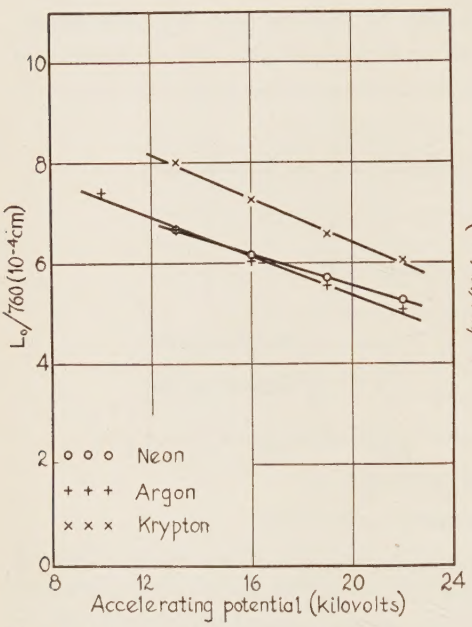

Fig. 4. Relationship between free path for ionization corrected to atmospheric pressure and accelerating potential for neon, argon, and krypton.

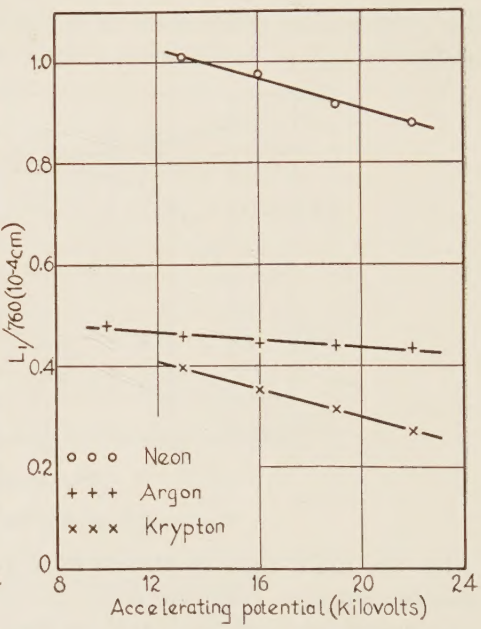

Fig. 5. Relationship between free path for neutralization corrected to atmospheric pressure and accelerating potential for neon, argon, and krypton.

and pressure were set by diminishing intensity; the upper limit of pressure was also set by diminishing intensity, apparently due to scattering; the upper velocity limit was determined by the voltage at which sparking began to occur inside the tube.

From Eqs. (1) and (3) it is seen that the equations expressing the dependence of the various measured quantities on pressure are

$$F_1 \text{ or } F_2 = e^{-py/L_0}\left[F_\infty + (1 - F_\infty)e^{-(1/L_0+1/L_1)px}\right], \tag{4}$$

$$F_3 = F_\infty e^{-py/L_0}\left[1 - e^{-(1'/L_0+1/L_1)px}\right] \tag{5}$$

where x is the distance from the point of origin of the beam to the beginning of the deflecting field and y the length of the field. The expressions for F_1 and F_2 differ only in the values of x and y. For F_1, $y=y_1=7.4$ cm, $x=x_1=0.75$ cm; for F_2, $y=y_2=1.1$ cm, $x=x_2=8.25$ cm; for F_3, $y=y_3=y_2=1.1$ cm, $x=x_3=14.55$ cm.

Since x_1 is small (0.75 cm) and y_1 relatively large (7.4 cm), the value of F_1 is almost completely independent of L_1 and F_∞. Therefore, a single measurement of F_1 is sufficient for the determination of L_0. In Fig. 2, the experimental points obtained in neon for two different voltages, 16,000 and 22,000 volts, are plotted. The curves shown are plotted from Eq. (4) with $L_0=0.470$ cm for 1 mm pressure for 16,000 volts, and $L_0=0.400$ cm for 22,000 volts. These curves show good agreement with the experimental points for all pressures. They show, also, the dependence of F_1 on voltage, the curve falling as the voltage was increased in all cases.

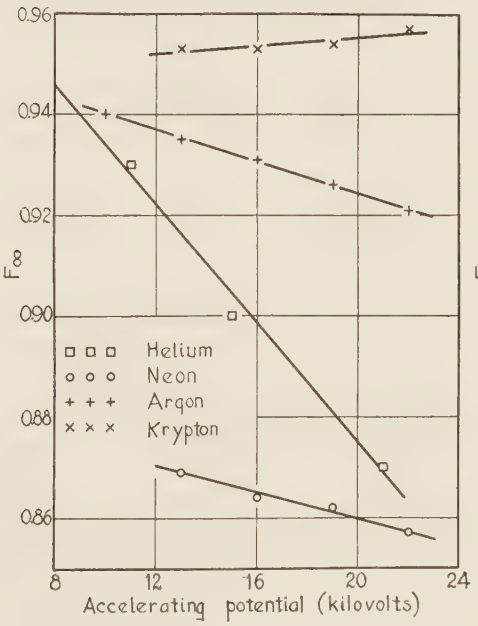

Fig. 6. Relationship between F_∞ and accelerating potential for helium, neon, argon, and krypton.

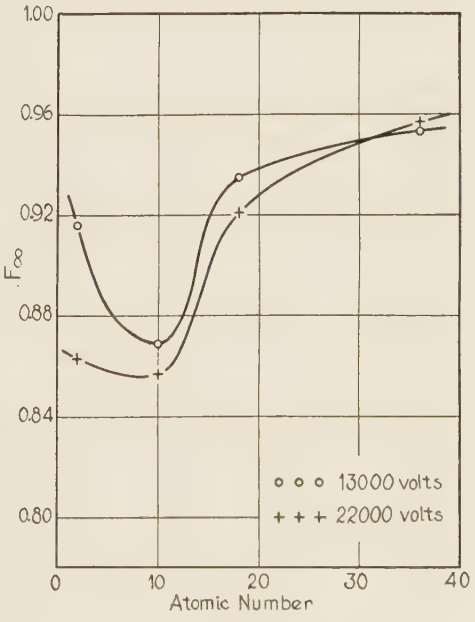

Fig. 7. Relationship between F_∞ and atomic number.

Having obtained the value of L_0 for a particular voltage, we find it possible to calculate the coefficient in front of the brackets in Eqs. (4) and (5) which arises from the decay of intensity in the short condenser. If we multiply the experimentally observed values F_2 and F_3 by e^{py_2/L_0} and denote the result by F_2', F_3', then the corrected experimental values should be connected with the free paths by the relations

$$F_2' = F_\infty + (1 - F_\infty)e^{-(1/L_0+1/L_1)px} \tag{6}$$

$$F_3' = F_\infty\left[1 - e^{-(1/L_0+1/L_1)px}\right]. \tag{7}$$

From these equations, it is seen that both F_2' and F_3' become equal to F_∞ for large pressures. In Fig. 3, the corrected experimental values at different pressures for 16,000 volts for neon have been plotted against pressure. The graph shows that F_2' and F_3' do approach the same constant value at high pressures as indicated by the equations. Thus, the value of F_∞ is obtained. L_1 may be determined from Eq. (2) with the values of L_0 and F_∞ already found.

This process was repeated to find the values of L_0, L_1, and F_∞ for each voltage used. The results are given in Table I. Column 3 gives the velocity corresponding to the accelerating potential given in column 2. Columns 4 and 5 show the mean free paths in centimeters corrected to atmospheric pressure of the neutral atoms and positive ions respectively. Column 6 contains the values of F_∞. The results of other observers and the kinetic theory values of the free paths are included for purposes of comparison. Figs. 4, 5, and 6

TABLE I.

1 Gas	2 Accelerating potential in volts	3 Velocity in cm per sec.	4 $L_0/760$ in cm	5 $L_1/760$ in cm	6 F_∞	7 Observer
Neon	22,000	4.58×10^7	5.3×10^{-4}	0.88×10^{-4}	0.86	
	19,000	4.16	5.7	0.91	0.86	
	16,000	3.91	6.2	0.98	0.86	
	13,000	3.52	6.7	1.01	0.87	
	400	0.62		0.34		Kallmann and Rosen[1]
			0.21			Kinetic theory value for 20°C and 760 mm
Argon	22,000	3.24×10^7	5.1×10^{-4}	0.44×10^{-4}	0.92	
	19,000	3.03	5.6	0.44	0.93	
	16,000	2.78	6.0	0.44	0.93	
	13,000	2.51	6.7	0.46	0.94	
	10,000	2.20	7.4	0.48	0.94	
	400	0.44		0.15		Kallmann and Rosen[1]
	200	0.31		0.13		Penning and Vennemans[3]
	837	0.64		0.067		Wolf[4]
	20 to 520	0.38		0.11		Wolf[4]
			0.11			Kinetic theory value for 20°C and 760 mm
Krypton	22,000	2.26×10^7	6.0×10^{-4}	0.27×10^{-4}	0.96	
	19,000	2.10	6.6	0.32	0.95	
	16,000	1.93	7.3	0.35	0.95	
	13,000	1.74	8.0	0.40	0.95	
			0.10			Kinetic theory value for 20°C and 760 mm

show the dependence of L_0, L_1, and F_∞, respectively, on accelerating potential. In Fig. 7, F_∞ is plotted as a function of atomic number for 13,000 and for 22,000 volts. The values for helium are taken from Rudnick's data.[11] The measurements at lowest voltages have been omitted from the table and graphs, since all measurements below 13,000 volts were difficult on account of small intensity. Particularly was this true at high pressures as scattering also decreased the intensity. Since the determination of F_∞ and L_1 depends on high-pressure measurements no reliable values could be obtained for low velocities. However, the readings made at lower pressures indicated no large changes in L_0, L_1, or F_∞ at these velocities.

Discussion of Results

The results of the preceding paragraph have been deduced from the observation of F_1 which gives L_0, the free path for ionization, and of F_∞, the equilibrium condition reached by the beam. L_1 has been deduced from the equilibrium value and not observed directly. The observations, however,

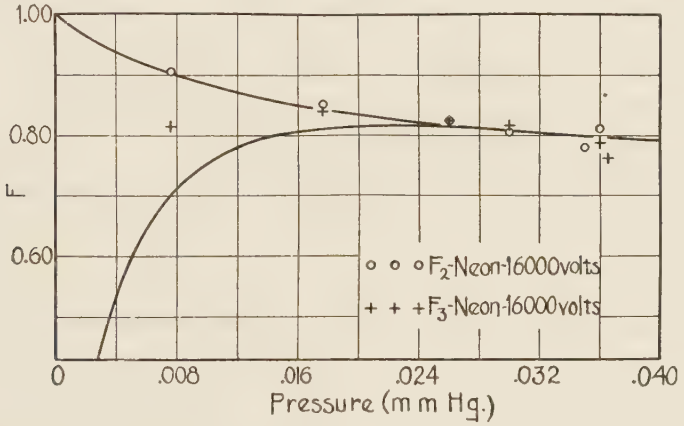

Fig. 8. Relationships between F_2 and pressure, and F_3 and pressure. Points shown are experimental values, curved are values plotted from Eqs. (4) and (5), respectively.

including the dependence of F_2 and F_3 on pressure, contain more data than are required to deduce L_0 and L_1, and may be used to check the adequacy of the theory to account for the dependence on pressure observed in the case of F_2 and F_3.

Having determined L_0, L_1, and F_∞ for any particular velocity, it is possible to plot complete curves for F_1, F_2, and F_3 from Eqs. (4) and (5) for comparison with the experimentally determined points. This has been done already for F_1 in Fig. 2. Fig. 8 is a similar comparison for F_2 and F_3. As in Fig. 2, the points shown are the observed values, the curves the theoretical values. Since L_0, L_1, and F_∞ were determined from the high-pressure data the agreement is necessarily good for these values of the pressure. It is seen that the agreement is good for F_1 and F_2 for all pressures, but that for F_3, for pressures less than 2×10^{-2} mm, the experimental points lie considerably above the curve plotted from Eq. (5). For argon and krypton the experimental

points for F_1 and F_2 also lie above the curves, but in no case is the deviation as great as for F_3. With increasing velocity the deviation decreases, being small for the highest velocities.

This deviation from the theoretical curves may be shown in another way. Given a set of values of F_1, F_2, and F_3 for a particular pressure and velocity, it is possible to solve Eqs. (4) and (5) for L_0, L_1, and F_∞, i.e., for each velocity it is possible to determine the required constants for a series of pressures. This has been done; the results are shown in Figs. 9 and 10. In Fig. 9, p/L_0 and in Fig. 10, p/L_1 are plotted against pressure. The graphs for neon for accelerating potentials of 16,000 and 22,000 volts are shown in each case. Since L_0 and L_1 are constants,—the free paths for 1 mm pressure—as expressed in the equations, p/L_0 *vs.* p and p/L_1 *vs.* p should both give straight lines through the origin. Actually the graphs are approximately straight lines but

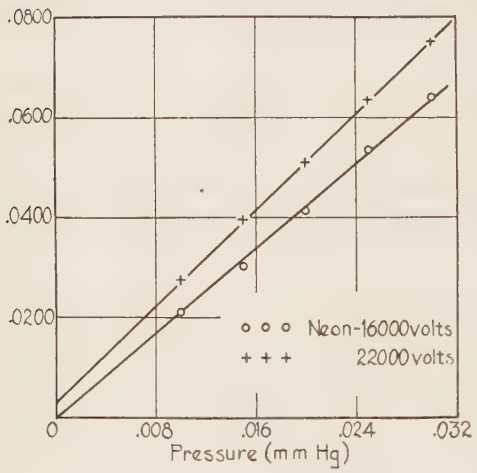

Fig. 9. Relationship between free path for ionization and pressure. Abscissa, p/L_0.

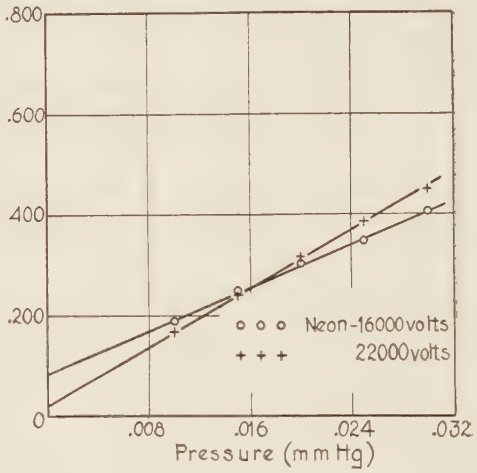

Fig. 10. Relationship between free path for neutralization and pressure. Abscissa, p/L_1.

do not pass through the origin. In Fig. 9 the displacement is small in both cases—probably less than experimental error. In Fig. 10, however, the displacement is much greater. The fact that it is smaller for 22,000 volts than for 16,000 volts corresponds to the fact that the agreement between experimental and theoretical values, shown in Fig. 8, is much better for the higher velocities. For argon and krypton, the straight lines of Fig. 9 are also displaced from the origin, since for these gases, the experimental values of F_1 and F_2 do not fall on the theoretical curves as they do in the case of neon, but here again the displacement decreases with increasing velocity.

Two arguments may be advanced to justify the calculation of the desired constants from the high-pressure data. First, the corrected curves for F_2 and F_3, shown in Fig. 3, do exhibit the properties expected at high pressures. Also, it is possible to obtain much better agreement between experimental and theoretical values by using the values of L_0 and L_1 determined for high rather than low pressures. The second is found in Rüchardt's work[8] with

hydrogen. His data also gave displaced straight lines like those shown in Figs. 9 and 10 when the reciprocals of the free paths were plotted against pressure. However, when the work was repeated, taking great precautions to eliminate all vapors, he obtained straight lines through the origin. He found that the lines obtained in the first case, were displaced considerably from the lines in the second case for low pressures, but that the displacement decreased with increasing pressure, i.e., the values for the free paths, as determined at high pressures, were the same in the two cases. In view of this work, it seems probable that the errors in the values given in Table I are not great.

Several explanations may be suggested for the disagreement between experimental and theoretical curves at low pressures. The fact that the discrepancy increases with decreasing velocity, and is greater for argon and krypton than for neon, suggests that scattering may have influenced the results since a comparison of total beam intensities at different velocities indicated that scattering increases with decreasing velocity and with increasing atomic number. This explanation is further supported by the fact that in some cases the corrected curves F_2' and F_3' of Fig. 3, do not reach a constant value, but appear to continue to decrease with increasing pressure. This can be explained by assuming that the neutral particles were scattered more than the ions. This decrease, however, is scarcely greater than experimental error in any case. An investigation of the effect of scattering shows that the results would depend only on the difference between the scattering coefficients of the atoms and ions, i.e., if they were scattered equally the results would be unaffected. Assuming a difference in scattering, we find that good agreement can be obtained between experimental and theoretical curves, but only when an unreasonably large difference in scattering coefficients is assumed—a difference so large that the intensity of the beam reaching the thermocouple would have been so small as to be quite undetectable. For this reason the scattering explanation seems to be ruled out. However, it should be pointed out that, while a small difference in the scattering of atoms and ions would not change appreciably the measured values of F_1, F_2, and F_3, the values of L_0, L_1, and F_∞, as calculated, might be very considerably in error if such a phenomenon were present.

It has been suggested that three rather than two types of particles may have been present in the beam, e.g., normal atoms, metastable atoms, and positive ions. An investigation of this possibility, with the necessary introduction of rather arbitrary assumptions about the processes involved, gives only slightly better agreement than the simple theory with the experimental values. This better agreement may, perhaps, be explained merely by the fact that another parameter is introduced into the equations; at least, the agreement obtained does not warrant any conclusions as to the correctness of the assumptions made.

In his work on hydrogen, Rüchardt[8] concluded that the observed discrepancies could be accounted for completely by the presence of vapors in the tube. In the present work, it does not seem unlikely that vapors were

present, despite the precautions taken, since a continuous flow of gas was not used. Further, Bartels[18] found that the fraction of neutral particles increased when the beam passed through a slit. This may be accounted for, probably, by the evolution of vapors due to bombardment of the edges of the slit. In the present work, vapors might be expected to be present for this reason also, since the beam passed through several circular diaphragms. The pressure of such vapors would be independent of the gas pressure in the tube. However, the number of collisions with vapor molecules relative to the number of collisions with gas atoms, would be greater at low pressures; therefore, the discrepancies introduced would be greater at these pressures. The observed deviations would be accounted for if the ions in the beam were more readily neutralized by collisions with the vapor molecules than with the gas atoms, since, in all cases, the fraction of neutral atoms in the beam at low pressures is greater than that expected from high-pressure measurements. On the whole, the presence of vapors seems to be the most reasonable explanation of the observed discrepancies, although it is quite probable that all the suggested phenomena and other more complex ones influence the measurements in some degree. If the discrepancies are accounted for by the presence of vapors, it seems likely that the values given in Table I, determined from the high-pressure measurements, are reasonably accurate. It may seem that the measurements for argon and krypton are much less reliable than for neon since the pressure range investigated was considerably lower, but in this connection, it should be noted that F_2 and F_3 became equal at much lower pressures with these gases than with neon and that the discrepancies observed were only slightly greater than with neon.

It will be seen from Figs. 4 and 5 that, for all the gases investigated in the present work, both free paths decrease slowly with increasing velocity. The behavior of helium differs in two respects; first, the rate of decrease of L_0 with increasing accelerating potential is much greater than for neon, argon, or krypton; secondly, for helium, L_1 increases rather than decreases as the velocity becomes greater. Fig. 7 shows a minimum value of F_∞ as a function of atomic number for both 13,000 and 22,000 volts, although it appears that for higher velocities this minimum would disappear. With reference to the dependence of F_∞ on atomic number, it may be noted further from Fig. 6 that the rate of change of F_∞ with velocity increases with atomic number from a relatively large negative value for helium to a small positive value for krypton. The increase of F_∞ with velocity for krypton, however, is small enough to be rather uncertain.

It is interesting to compare the measured values of the free paths with the kinetic theory values. A comparison shows that for neon the kinetic theory free path is about one-thirtieth of the free path for ionization of a high-velocity atom and about one-fifth of the free path for the neutralization of a fast ion, i.e., a moving atom is ionized at about every thirtieth collision with a rest atom and a moving ion is neutralized at about every fifth collision.

[18] H. Bartels, reference 9, p. 969.

In argon, the probability of ionization is less, occurring for approximately one collision in sixty, but the probability of neutralization is about the same. With krypton, ionization takes place at every seventieth collision, approximately, while neutralization occurs for one collision in four.

A comparison of the free paths of the ions in the present work, with those obtained from the low-velocity measurements of Kallmann and Rosen[1] and others[3,4] shows that the values for high velocities are approximately three times those for the slow ions in all cases. Since Fig. 5 shows a decrease of L_1 with increasing velocity, for neon, argon, and krypton, the comparison might suggest that the free path for neutralization for these gases, has a maximum for some accelerating potential intermediate between 800 and 7000 volts. This is not a necessary conclusion, however, as the difference in the method of measurement makes the comparison doubtful. In the present work only a difference in the scattering of the atoms and ions would affect the results, whereas with the method used in the low-velocity measurements, any scattering of ions would result in a decrease of the intensity of the ionic beam, and, therefore, in a decrease of the measured free path. It seems probable that scattering would be relatively large for the slow ions, particularly in view of the conclusion of Kallmann, Lasareff, and Rosen in a recent article[19] that slow neutral atoms are scattered at every kinetic theory collision. The difference in the values obtained may, perhaps, be completely explained by the effect of scattering in the low-velocity measurements.

Doppler effect observations of positive rays of neon[12,13] and argon[13,14] of velocities similar to those used in the present work show a surprising absence of displaced arc lines. This fact might be interpreted as proof that the particles in the beam are predominantly positive, the absence of neutral atoms accounting for the absence of displaced arc lines. This suggestion is supported by the work of Rutherford[20] and Henderson[21] in which they found that neutral atoms are present in an α-ray beam only at lower velocities. The present experiments show, however, that in neon 86 percent of the particles in the beam are neutral, while in argon 93 percent and in krypton 95 percent are neutral. This seems to rule out the suggested interpretation. The alternative interpretation appears to be that, for some reason, after a collision a moving particle is seldom, if ever, left in an excited neutral state.

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